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X.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE REACTIONS OF SODIC ALCOHOLATES WITH TRIBROMDINITROBENZOL AND TRIBROMTRINITROBENZOL.

By C. Loring Jackson and W. H. Warren.

Presented May 27, 1890.

We were induced to take up this piece of work — although at first sight it might seem to promise little of interest, either in the new compounds formed or in the nature of the reaction — by some experiments in a previous research which apparently indicated that one of the atoms of bromine in tribromdinitrobenzol would be replaced by hydrogen under the influence of sodic ethylate. If this was the case, the work would supply additional material on which to found an explanation of the substitution of bromine by hydrogen in the formation of bromdinitrophenylmalonic ester and allied compounds, described in several previous papers * from this Laboratory. Not only has the promise of these experiments been fulfilled, but the work has surpassed in interest all that we expected of it, as it has shown that sodic alcoholates (under which name we class phenolates also) act on tribromdinitrobenzol and tribromtrinitrobenzol in four different ways: —

First. A simple replacement of each atom of bromine by the radical of the alcoholate. This we have observed only in a single case, the action of sodic phenolate on tribromtrinitrobenzol giving trinitrophloroglucine triphenylether, $C_6(NO_2)_3(OC_6H_5)_3$, melting point 175°.

Second. The replacement of two atoms of bromine by two of the radical of the alcoholate, the third atom of bromine remaining unaltered. Under this head come the actions of sodic ethylate in the cold, methylate (in part), and phenolate on tribromdinitrobenzol, giving $C_6HBr(C_2H_5O)_2(NO_2)_2$, melting point 184°, $C_6HBr(CH_3O)_2(NO_2)_2$, melting point 237°–238°, and $C_6HBr(C_6H_5O)_2(NO_2)_2$, melting point 165°.

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* These Proceedings, xxiv. 1, 256, 271, 288, 306 (1888–89).

Third. The replacement of two atoms of bromine by the radical of the alcoholate, and the third by hydrogen. Sodic ethylate when hot, and sodic methylate (in part) whether cold or hot, act in this way on tribromdinitrobenzol, giving $C_6H_2(C_2H_5O)_2(NO_2)_2$, melting point 133°, and $C_6H_2(CH_3O)_2(NO_2)_2$, melting at 167°. These substances can also be made by boiling the corresponding bromine compounds (mentioned under the second class) with the proper alcoholate.

Fourth. The replacement of one, two, or perhaps three of the nitro groups by the radical of the alcoholate, the three bromine atoms remaining unaffected. This very strange action was observed with sodic ethylate or methylate and tribromtrinitrobenzol, giving $C_6Br_3C_2H_5O(NO_2)_2$, melting point 147°, $C_6Br_3(C_2H_5O)_2(NO_2)$, melting point 101°, and $C_6Br_3(CH_3O)_2(NO_2)$, melting point 126°.

The product of further action of sodic ethylate when hot, on tribromnitroresorcine diethylether has not yet been obtained in a state of purity, but we hope to be able to describe it in a later paper.

We have little to say in general about these different modes of action of the alcoholates, except to connect them with previous observations of a similar character, as we think that the number of facts established is still insufficient for the safe foundation of a theoretical explanation of these differences. We hope to continue the work, however, until such a foundation has been secured. The formation of the trinitrophloroglucine triphenylether (described under the first head) is analogous to the formation of trinitrophenylenedimalonic ester from the bromtrinitrophenylmalonic ester,* since in the corresponding dinitro compounds the third atom of bromine cannot be replaced by the phenoxy (see second head) or malonic ester radical, as the case may be, even under more powerful inducements than are needed to bring about this action with the trinitro compounds, thus furnishing another example of the loosening effect of the presence of a third nitro group upon the bromine. The stability of the third atom of bromine in the dinitro compound, so far as replacement by an alcoholate radical is concerned, mentioned under the second head, is analogous to that of the third bromine atom in dinitrobromphenylmalonic† or acetacetic‡ ester in the corresponding dinitrodibrom compound,* and to a less extent in the trinitro derivative †; while the replacement of bromine by hydrogen, mentioned under the third head, corresponds closely to the removal of the second atom of bromine from all these substances. In regard to the replacement of the nitro groups instead of the atoms of bromine by ethoxy or methoxy radicals, described under the fourth head, we can only say that the conditions were essentially the same as those under which the bromine in the dinitro compound was replaced, and that as yet we have no hint of an explanation for it, but hope that future experiments will throw some light on the cause of this strange behavior. We may here call attention to the fact, that the replacement of these nitro groups is in direct contradiction to Laubenheimer's rule,‡ that a nitro group is removed only when it is in the ortho position to another nitro group, since in the tribromtrinitrobenzol the three nitro groups are in the meta position to each other. Whether this exception to Laubenheimer's rule is due to the fact that it does not apply to sodic ethylate, or to some cause peculiar to the tribromtrinitrobenzol, must be determined by future experiment.

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* These Proceedings, xxiv. 268.

† Ibid., 2.

‡ Ibid., 274.

We also found that neither sodic acetate nor sodic picrate acted on tribromdinitrobenzol even at 100°, nor did sodic picrate act on tribromtrinitrobenzol, which justifies the inference that decidedly acid radicals cannot be taken up by these molecules, which contain so many nitro groups. Also we have repeated the experiment on the action of malonic ester upon tribromdinitrobenzol and confirm the negative results previously obtained.§

The description of the experimental details of the research occupies the rest of the paper.

Action of Sodic Ethylate on Tribromdinitrobenzol in the Cold.

In order to study this action 20 gr. of tribromdinitrobenzol (melting point 192°, made from symmetrical tribrombenzol) dissolved in a mixture of 40 c.c. of benzol and 90 c.c. of absolute alcohol were treated with an alcoholic solution of the sodic ethylate, made from 3.4 gr. of sodium, which gave the proportion of three molecules of sodic ethylate to one of tribromdinitrobenzol. That a reaction took place was indicated by the appearance of a pale reddish yellow color, which gradually increased in intensity to a dark brownish red, but there was no perceptible evolution of heat. To give the reaction time to run to an end, the mixture was allowed to stand in a corked flask at ordinary temperatures for two or three days, and then was filtered to remove a considerable amount of solid matter which had separated, and the filtrate allowed to evaporate spontaneously. The solid remaining on the filter was washed with water to remove sodic bromide, the presence of which was proved by testing this wash water with argentic nitrate after acidification with nitric acid, and the portion insoluble in water added to the main product when that had been brought to the same degree of purity. This main product was deposited from the filtrate by the spontaneous evaporation of the solvent, and after washing with water was purified by crystallization from hot alcohol until it showed the constant melting point 184°. It is worth mentioning that the earlier crystallizations yielded round woolly masses of fine needles, which were gradually converted, as the substance approached purity, into well formed prisms or plates, since this change in the crystalline habit furnishes a convenient indication of the comparative purity of the substance. The analyses of the substance dried at 100° gave the following results: —

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* These Proceedings, xxiv. 294.

† Ibid., 258.

‡ Ber. d. ch. G., ix. 766, 1828.

§ These Proceedings, xxiv. 308 (1889).

I. 0.2616 gr. of the substance gave on combustion 0.3426 gr. of carbonic dioxide and 0.0904 gr. of water.

II. 0.2753 gr. of the substance gave 21.9 c.c. of nitrogen at a temperature of 25° and a pressure of 745.5 mm.

III. 0.1830 gr. of the substance gave according to the method of Carius 0.1032 gr. of argentic bromide.

	Calculated for $C_6HBr(C_2H_5O)_2(NO_2)_2$.	Found.		
		I.	II.	III.
Carbon	35.83	35.72		
Hydrogen	3.28	3.84		
Nitrogen	8.36		8.70	
Bromine	23.89			24.00

There can be no doubt, therefore, that this substance melting at 184° is the bromdinitroresorcine diethylether formed by the replacement of two atoms of bromine by two of the ethoxy radicals.

The yield of bromdinitroresorcine diethylether is far from good, 20 gr. of tribromdinitrobenzol giving in no instance more than 4.6 gr. of this substance instead of the 16.5 gr. required if the whole of the tribromdinitrobenzol had been converted into it, that is, about 28 per cent; and, in fact, the alcoholic mother liquors from its purification yielded on evaporation a viscous residue in large quantity, our unsatisfactory work upon which will be described after the statement of the properties of the bromdinitroresorcine diethylether. We may give here, however, the result of a determination of the amount of sodic bromide formed in the reaction. 5 gr. of tribromdinitrobenzol were treated in the cold with the sodic ethylate from 0.9 gr. of sodium in the manner described above, and, after the reaction had come to an end, water was added, the benzol solution removed, and the water extracted three times with benzol, after which it was made up to a volume of 500 c.c., and the amount of sodic bromide determined in 20 c.c. of this solution; the weight thus obtained calculated on the whole solution gave the result given below as found. The calculated number is the amount of sodic bromide which would be formed if two of the atoms of bromine in the tribromdinitrobenzol had been removed.

	Calculated.	Found.
Sodic Bromide	1.271 gr.	1.194 gr.

These results agree as closely as could be expected considering the unavoidable losses in extracting with benzol, and prove that in this case two of the atoms of bromine contained in the tribromdinitrobenzol were removed as bromide of sodium.

Properties of Bromdinitroresorcine Diethylether, $C_6HBr(C_2H_5O)_2(NO_2)_2$.

The substance crystallizes from alcohol in rather thick flattened needles of a yellowish white color, which may attain a length of 1 cm. and sometimes a breadth of 1 mm. The ends are usually square, but less often consist of two planes at a very obtuse angle to each other. The larger crystals seem to be made up of needles united longitudinally, since their ends are apt to be sharply serrated, or even as much indented as the teeth of a comb. Crystallized from benzol it formed long slender prisms, sometimes reaching a length of 2 cm., terminated by two planes at an acute angle to each other, and efflorescing on exposure to the air. They showed however the same melting point as the crystals obtained from alcohol, and when recrystallized from this solvent gave the plates with square ends described above; they probably contained benzol of crystallization, which escaped before the temperature had risen to the melting point of the substance. It melts at 184°; and is not very soluble in alcohol even when hot, less so when cold; slightly soluble in methyl alcohol; nearly insoluble in cold water, very slightly soluble in hot; freely soluble in acetone; soluble in benzol or chloroform; slightly soluble in ether or glacial acetic acid; nearly insoluble in carbonic disulphide; and insoluble in ligroine. Alcohol, or alcohol with a little benzol, is the best solvent for it. Neither sulphuric, nitric, nor hydrochloric acid has any apparent action on it, whether cold or hot.

As has been already stated, the alcoholic mother liquors from the crystallization of the bromdinitroresorcine diethylether yielded on evaporation a semi-liquid mass of most uninviting properties in considerable quantity; but although we have given much time to the study of this product, we are unable to make any definite statement in regard to its nature, and have not thought it worth while to postpone the printing of this paper until we could overcome the difficulties in its purification, as it does not lie in the direct line of our research, the principal object of which has been reached by our work on the bromdinitroresorcine diethylether and its derivatives. We think it well, however, to give a brief statement of our work on this secondary product, since we have succeeded in isolating a crystalline substance from this viscous mixture by a process of liquation, which we think will prove of value to those chemists who have similar mixtures to deal with. The viscous mass after standing for some weeks solidified, but even then was deposited from all its solutions in its original oily condition, and as therefore it could not be crystallized directly we proceeded as follows. Having found that about one quarter of it melted at 50°–60°, we placed it on several layers of filter paper in a dish heated to about 70° by means of a water bath, and allowed it to stand at this temperature for several days, renewing the filter paper as it was necessary, and toward the end of the process applying a gentle pressure. The less fusible residue thus obtained could now be crystallized from alcohol, and yielded a small quantity of a substance melting near 170°, which we took to be impure bromdinitroresorcine diethylether, but the amount was so small that we could not recrystallize it often enough to raise the melting point to the proper temperature, 184°. The principal part of this less fusible portion melted in the neighborhood of 150°, and proved to be a mixture which, to judge by the melting point, was the same as an abnormal product occasionally obtained from the process for making bromdinitroresorcine diethylether instead of that substance, although we could find no difference in the conditions of the process from those when it gave the normal result. We have not succeeded in separating this mixture into its components, as after several unsuccessful experiments the amount remaining at our disposal was too small to continue with any prospect of success the crystallizations, which seemed to purify it very slowly, as they had but little effect on the melting point. Some analyses of the mixture showed that it contained less carbon and more bromine than bromdinitroresorcine diethylether.

The more fusible portion of the secondary product, which had been absorbed by the papers in the process of liquation, was extracted with alcohol, and the oil thus obtained allowed to stand until it had nearly solidified again, when it was submitted to a second liquation, the more fusible product of which did not solidify, but only deposited a few crystals. As there were only about 10 gr. of this in all, and it manifestly contained two, and in all probability three or more substances we thought there would be little chance of isolating a pure compound from it, and accordingly, after one or two attempts to separate it into its components, its further study was abandoned.

Action of Sodic Ethylate on Tribromdinitrobenzol with the Aid of Heat.

As has been shown in the preceding section, sodic ethylate acting on tribromdinitrobenzol (melting point 192°) in the cold converts it into bromdinitroresorcine diethylether melting at 184°; but if, instead, the two substances are heated together, a different product is obtained which we have found it most convenient to prepare in the following way.

A solution of 10 gr. of tribromdinitrobenzol (melting point 192°) in 20 c.c. of benzol was mixed with the alcoholic solution of sodic ethylate formed from 45 c.c. of alcohol and 1.7 gr. of sodium, giving the proportion of three molecules of the ethylate to one of the tribromdinitrobenzol, and the mixture was heated on the steam bath to gentle boiling for about ten minutes in a flask under a return condenser. Longer or more violent heating should be avoided, as in this case a decomposition sets in, probably due to the action of the sodic ethylate on the nitro groups, which increases the difficulty in purifying the product. During the boiling the red color of the solution steadily increased in intensity, and a considerable amount of sodic bromide was deposited together with a brown amorphous substance which added to the turbidity of the reddish brown liquid finally obtained. A curious odor was also observed in the solution, which seemed to be characteristic of all the reactions in which bromine was replaced by hydrogen, and was probably due to the secondary product formed from the sodic ethylate, but did not smell like the aldehyd which we had supposed would be this secondary product by the following reaction: —

$$C_2H_5ONa + C_6HBr(C_2H_5O)_2(NO_2)_2 = NaBr + C_6H_2(C_2H_5O)_2(NO_2)_2 + C_2H_4O.$$

At the end of the ten minutes the solution was poured into an evaporating dish and allowed to evaporate to dryness spontaneously, washed with water to remove sodic bromide, and the reddish brown substance insoluble in water purified by crystallization from alcohol with the aid of boneblack until it showed the constant melting point 133°, when it was dried at 100°, and analyzed with the results given under I. and III. More than a year ago G. D. Moore with one of us obtained under somewhat different conditions the same substance as shown by the melting point and crystalline form, and we therefore add the analyses made of it by Dr. Moore at that time, II., IV., and V.

I. 0.2200 gr. of the substance gave on combustion 0.3752 gr. of carbonic dioxide and 0.0950 gr. of water.
II. 0.2320 gr. of the substance gave 0.3990 gr. of carbonic dioxide and 0.0995 gr. of water.
III. 0.2112 gr. of the substance gave 21 c.c. of nitrogen at a temperature of 26° and a pressure of 754.8 mm.
IV. 0.2299 gr. of the substance gave 22.3 c.c. of nitrogen at a temperature of 23° and a pressure of 762.2 mm.
V. 0.2142 gr. of the substance gave 20.3 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 767 mm.

	Calculated for $C_6H_2(C_2H_5O)_2(NO_2)_2$.	Found.				
		I.	II.	III.	IV.	V.
Carbon	46.88	46.50	46.90			
Hydrogen	4.69	4.80	4.77			
Nitrogen	10.94			10.96	10.96	10.81

It contained no bromine.

These analyses prove that the substance is the dinitroresorcine diethylether which must have been formed from the tribromdinitrobenzol $C_6HBr_3(NO_2)_2$ by the replacement of two of its atoms of bromine by two ethoxy radicals (C_2H_5O), the third by hydrogen, and we have here another case of the curious replacement of bromine by hydrogen in preference to its replacement by a radical combined with sodium, which was first observed in the study of the action of sodium malonic ester upon tribromdinitrobenzol, and which induced us to undertake the present investigation. Since this dinitroresorcine diethylether melts at 133°, it is isomeric with the one[*] already known melting at 75°.

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[*] Aronheim, Ber. d. ch. G., xii. 32.

Properties of Dinitroresorcine Diethylether, $C_6H_2(C_2H_5O)_2(NO_2)_2$. —This substance crystallizes by cooling from an alcoholic solution in long slender needles or flattened prisms with a sharp point. If the alcoholic solution is allowed to evaporate spontaneously, it forms some curling hair-like crystals which are very characteristic. The crystals from alcohol are also apt to form clumps of radiating hairs shaped somewhat like a toadstool, especially if the substance is not absolutely pure. From ether it crystallizes in needles combined longitudinally into prisms with prickly ends; from chloroform, in radiating needles. It melts at 133°, and is nearly insoluble in water, although apparently a little more soluble in it hot than cold; not very soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; freely soluble in chloroform, glacial acetic acid, or acetone; soluble in benzol; slightly soluble in ether; very slightly in carbonic disulphide; essentially insoluble in ligroine. Alcohol is the best solvent for it. Strong sulphuric acid dissolves it in the cold, forming a yellow solution; strong nitric acid has no action on it when cold, but gives a colorless solution if heated with it; strong hydrochloric acid has no action on it, whether hot or cold.

Conversion of Bromdinitroresorcine Diethylether into Dinitroresorcine Diethylether.

It has been shown in the two preceding sections that the action of sodic ethylate on tribromdinitrobenzol differs according to the conditions under which it takes place, since in the cold bromdinitroresorcine diethylether is formed, but when the mixture is heated the third atom of bromine is also removed and replaced by hydrogen, so that the product is the dinitroresorcine diethylether. In order to throw more light on this substitution of hydrogen for the third atom of bromine we next tried the action of sodic ethylate when heated on the bromdinitroresorcine diethylether, as it was possible that this substitution could take place only at the moment of the replacement of the other two atoms of bromine by the ethoxy radicals, and in that case boiling sodic ethylate would not convert the ready formed bromdinitroresorcine diethylether into the dinitroresorcine diethylether. Accordingly 3 gr. of bromdinitroresorcine diethylether were mixed with the sodic ethylate from 0.6 gr. of sodium dissolved in alcohol,* and the mixture heated to gentle boiling for about ten minutes in a flask under a return condenser, when it had taken on a dark red color, and the curious odor observed in making the dinitroresorcine diethylether was very perceptible. The solvent was then allowed to evaporate spontaneously, and the residue washed with water, which removed sodic bromide (as was proved by the addition of argentic nitrate) and a red impurity. It was then purified by crystallization from hot alcohol, until it showed a constant melting point, when we found that this treatment had lowered the melting point from 184°, that of the bromdinitroresorcine diethylether, to 133°, that of the dinitroresorcine diethylether, which substance the product also resembled in appearance and solubility. To remove all doubt about its nature it was dried at 100° and analyzed, with the following results: —

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* We found that benzol must not be added in this case, as it seemed to interfere with the progress of the reaction.

0.1378 gr. of the substance gave on combustion 0.2354 gr. of carbonic dioxide and 0.0616 gr. of water.

	Calculated for $C_6H_2(C_2H_5O)_2(NO_2)_2$.	Found.
Carbon	46.88	46.58
Hydrogen	4.69	4.97

This proves that the substance is the dinitroresorcine diethylether, and that the principal action of the hot sodic ethylate upon the bromdinitroresorcine diethylether was the replacement of its bromine by hydrogen.

After the experiment just described had proved that the bromine in bromdinitroresorcine diethylether could be replaced by hydrogen by means of boiling sodic ethylate, it seemed of interest to determine whether the same change could be brought about by other reagents, and we tried first alcohol alone, which might produce this action by giving aldehyd and hydrobromic acid as secondary products, although this was not at all probable since the bromdinitroresorcine diethylether was purified by crystallization from hot alcohol; and indeed, after boiling it with alcohol for a long time in a flask under a return condenser, the result was entirely negative, nothing but unaltered bromdinitroresorcine diethylether melting at 184° being obtained on evaporation of the alcoholic solution.

From the action of malonic ester on bromdinitroresorcine diethylether we expected better results, because, although it is true that malonic ester has no action on tribromdinitrobenzol (see these Proceedings, xxiv. 308, and the concluding section of this paper), in the formation of bromdinitrophenylmalonic ester it seems to replace one atom of bromine by hydrogen in the dibromdinitrophenylmalonic ester* (which we must infer is an intermediate product in the reaction), and if this replacement is made possible by the presence of the malonic ester radical $CH(COOC_2H_5)_2$ in the molecule, we thought that perhaps the two ethoxy radicals in bromdinitroresorcine diethylether might produce the same effect. The result of the experiment, however, was again negative, whether carried on cold or hot, as the solid product melted at 184°; and the same result was obtained if acetacetic ester was used instead of malonic ester, although in this latter case the substances were boiled together for four hours.

Supposing from the negative results of these experiments that the presence of sodium malonic ester as well as malonic ester was necessary for the replacement of bromine by hydrogen in the hypothetical dibromdinitrophenylmalonic ester, (leading to an immediate formation of acetylenetetracarbonic ester † as the secondary product,) we tried the action of such a mixture, that is, one molecule of malonic ester to one molecule of sodium malonic ester, upon the bromdinitroresorcine diethylether in alcoholic solution, at first in the cold for five days, that is, under the conditions used in the preparation of bromdinitrophenylmalonic ester, but at the end of this time no sodic bromide could be detected, and essentially all the original ether was recovered unaltered. In another experiment the mixture was heated on the steam bath for fifteen minutes, but, although a distinct red color appeared, the reaction could have been at best a very limited one, as essentially all the bromdinitroresorcine diethylether was recovered unaltered, so that the new substance, if any were formed, was present in such small quantity that we were unable to detect it. It follows from these experiments, that the atom of bromine in bromdinitroresorcine diethylether is more firmly attached to the molecule than the second atom of bromine in the hypothetical dibromdinitrophenylmalonic ester, since this is replaced by hydrogen through the agency of malonic and sodium malonic esters, or more probably by the malonic ester alone considering the formation of tartronic acid. ‡

Action of Sodic Methylate on Tribromdinitrobenzol.

We took up this subject because it was possible that the action of sodic methylate might be different from that of sodic ethylate described in the preceding sections; but we have found that this is not the case, unfortunately at an expense of time and labor entirely out of proportion to the value of the results obtained.

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* These Proceedings, xxiv. 239.

† Ibid., 265.

‡ Ibid., 238.

Our experience with sodic ethylate induced us at first to try the action of sodic methylate in the cold; but as we soon found that the same products were obtained when the action was assisted by heat, we have usually proceeded in this way, since, when boiling, the reaction runs to an end in ten minutes, whereas in the cold it takes about two days. Finally we adopted the following method. 10 gr. of tribromdinitrobenzol dissolved in about 20 c. c. of benzol were mixed with a solution in methyl alcohol of the sodic methylate from 1.7 gr. of sodium, and the mixture boiled for ten minutes on the steam bath in a flask fitted with a return condenser, when a clear red solution was obtained, which on cooling deposited white crystals. These were filtered out, the filtrate allowed to evaporate to dryness, and the residue and crystals extracted three or four times with small amounts of hot alcohol, as in this way a viscous impurity was removed, the nature of which will be considered later. The purification of the less soluble portion offered great difficulties, which was the more surprising because it was but slightly soluble in any solvent, so that the separation of it from the viscous product was very easy, and by crystallization from hot alcohol we soon obtained a substance showing the constant melting point 237°–238°; but the results of its analysis did not agree with those calculated for bromdinitroresorcine dimethylether, as is shown by the following comparison: —

	Calculated for $C_6HBr(NO_2)_2(OCH_3)_2$.	Found.
Carbon	31.27	32.78
Hydrogen	2.28	3.21
Nitrogen	9.12	10.64
Bromine	26.05	25.02

As these analyses seemed to indicate that the substance was not pure, we crystallized it again several times, using glacial acetic acid as the solvent; and after a new set of analyses had yielded no better results than those given above, we recrystallized six or seven times, this time from acetone, but with no better agreement of the percentages derived from analysis with those corresponding to the formula. As the substance crystallized very well, we were inclined to think at first that we had a compound different from the bromdinitroresorcine dimethylether, probably with a higher molecular weight. Accordingly, we tried to determine the molecular weight of the substance by the method of Raoult, and obtained numbers not too far removed from the molecular weight of bromdinitroresorcine dimethylether; but we do not think these results of any value, as the solubility of the substance in glacial acetic acid was so slight that the differences in the depression of the freezing point for different molecular weights fell almost within the limits of error of the process. After many other experiments to determine the nature of this substance, which led to no result, we found at last in the anilido compound derived from it a body which could be purified by crystallization, and from the analysis of which a safe inference could be drawn in regard to the nature of the substance melting at 237°–238°.

Anilidodinitroresorcine Dimethylether,
$C_6H(C_6H_5NH)(CH_3O)_2(NO_2)_2$.

This substance was prepared by heating the body melting at 237°–238° with an excess of aniline to a temperature somewhat above 100° for about twelve hours, when the product was acidified with dilute sulphuric acid, washed carefully with water till all aniline salts were removed, and purified by crystallization from hot alcohol until it showed the constant melting point 196°. During this crystallization we observed indications that we were dealing with a mixture, as the constant melting point 196° was reached only when working with large quantities, and after repeated crystallization; but the impurity which seemed to melt near 206° was present in such small quantity that we were unable to determine its nature. The pure anilido compound was dried at 100°, and analyzed with the following results: —

I. 0.2973 gr. of the substance gave on combustion 0.5733 gr. of carbonic dioxide and 0.1167 gr. of water.
II. 0.2064 gr. of the substance gave 23.7 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 761 mm.

	Calculated for $C_6H(C_6H_5NH)(CH_3O)_2(NO_2)_2$.	Found.	
		I.	II.
Carbon	52.66	52.59	
Hydrogen	4.08	4.36	
Nitrogen	13.16		13.02

From this it appears that the anilido compound is anilidodinitroresorcine dimethylether, and consequently that the substance melting at 237°–238° must be essentially the bromdinitroresorcine dimethylether, but that it contains some impurity, which cannot be removed from it even by very long continued crystallization from alcohol, glacial acetic acid, or acetone; and this view is confirmed by the behavior of the anilido compound on crystallization described above. Another determination of the nature of the substance melting at 237°–238° will be given below, when we describe its conversion into dinitroresorcine dimethylether. The fact that in the action described above only the bromine was replaced by the aniline radical C_6H_5NH surprised us, as we had expected that the methoxy groups would undergo a similar replacement owing to their position in regard to the nitro groups.

Properties of Anilidodinitroresorcine Dimethylether, $C_6H(C_6H_5NH)(CH_3O)_2(NO_2)_2$.

This substance forms bright yellow needles, or very slender prisms, which show some tendency to unite in radiating groups. It melts at 196°, and is nearly but not quite insoluble in water; not very soluble in cold ethyl or methyl alcohol, more soluble in hot; freely soluble in chloroform or acetone; soluble in benzol or glacial acetic acid; slightly in ether; very slightly in carbonic disulphide, and insoluble in ligroine. Alcohol is the best solvent for it.

Properties of Bromdinitroresorcine Dimethylether, $C_6HBr(CH_3O)_2(NO_2)_2$.

Although we did not succeed in getting this substance absolutely pure, we think it worth while to give its properties, as the slight amount of impurity present could have influenced them but little, and they differ rather strikingly from those of the corresponding ethyl compound. When crystallized from glacial acetic acid by cooling, it forms prisms terminated by a single rhombic plane at an acute angle to the sides of the prism, which are so short that the crystal looks almost like a rhombohedron; these crystals are white with a faint yellowish tinge, and often a millimeter long. When crystallized by slow evaporation of the glacial acetic acid solution the crystals are converted into long well formed prisms, and the single rhombic plane which forms the principal termination is usually modified by other smaller planes. The highest melting point which we have obtained for this substance was 237°–238°, but the analyses showed that even when melting at this point it was still far from pure. It is nearly insoluble in water, its solubility being perhaps somewhat increased by boiling; very slightly soluble in ethyl or methyl alcohol, the solubility somewhat increased by heat; slightly soluble in acetone, benzol, chloroform, glacial acetic acid, or nitro-benzol; very slightly in ether or carbonic disulphide; insoluble in ligroine. The best solvent for it is acetone or glacial acetic acid, as it is more soluble in these liquids than in any other; but its slight solubility in all the common solvents is one of its most striking properties.

Dinitroresorcine Dimethylether, $C_6H_2(CH_3O)_2(NO_2)_2$.

This substance was formed in addition to the bromdinitroresorcine dimethylether by the action of sodic methylate in methyl alcoholic solution upon tribromdinitrobenzol, whether the substances were heated together, or the action was allowed to take place in the cold. The action of sodic methylate, therefore, on account of this indifference to the effect of temperature, is unlike that of sodic ethylate, which gave only bromdinitroresorcine diethylether in the cold, and when heated only dinitroresorcine diethylether. The dinitroresorcine dimethylether, which was formed in comparatively small quantity, was obtained from the alcoholic washings and mother liquors of the substance melting at 237°–238°. The residue left after the evaporation of the alcohol was a viscous mass, which contained in addition to the substance of which we were in search an oily impurity similar to that obtained from the ethyl compound and a little bromdinitroresorcine dimethylether. It was therefore a matter of some difficulty to isolate a pure substance from it, but we finally succeeded by repeated crystallization from hot alcohol, during which crystals of two sorts were obtained, one consisting of white needles turning brown in the air, the other of lemon-yellow rhombic crystals, which appeared especially during the earlier parts of the crystallization, and were gradually converted into the white needles. That the difference between the two forms consisted in the presence of one molecule of alcohol of crystallization in the white needles was shown by the following analytical results: —

I. 0.9817 gr. of the air-dried substance lost 0.0177 gr. at 100°.
II. 0.7617 gr. of the substance dried *in vacuo* lost 0.0142 gr. at 100°.

	Calculated for $C_6H_2(CH_3O)_2(NO_2)_2C_2H_5OH$.	Found. I.	 II.
Alcohol .	16.79	18.03	18.64

These numbers agree somewhat better with the percentages calculated for three molecules of *water* of crystallization; but, apart from the improbability that the substance would take up water when crystallized from ordinary alcohol, we have found that the liquid given off, when the needles were heated in a test tube, dissolved the crystals clinging to the side of the tube, and that the substance dried at 100°, when recrystallized from absolute alcohol, gave white prisms like those whose analysis is given above. The analysis which follows was made with the white needles after they had been dried at 100°, and therefore freed from their alcohol of crystallization.

0.2688 gr. of the substance gave on combustion 0.4092 gr. of carbonic dioxide and 0.1027 gr. of water.

	Calculated for $C_6H_2(CH_3O)_2(NO_2)_2$.	Found.
Carbon	42.11	41.52
Hydrogen	3.51	4.25

The substance contains no bromine.

From these results it is evident that the substance is the dinitroresorcine dimethylether, but its melting point, 167°, shows that it is isomeric with the substance * of this composition already known, which melts at 67°.

Properties. — The dinitroresorcine dimethylether was obtained crystallized with one molecule of alcohol, and also in crystals free from alcohol. When containing a molecule of alcohol it forms sheaves or bunches of white needles, or slender prisms often a centimeter long terminated by two planes at a very obtuse angle to each other, or less often a single plane at an acute angle to the sides; frequently also a single plane at right angles to the sides was observed, but we were inclined to consider this due to cleavage rather than a real termination of the crystal. These two prevailing forms, the two planes at an obtuse angle, and the single plane at a right angle, give a general square-ended effect to the crystals which is characteristic. On exposure to the air these crystals turn purplish brown. When containing no alcohol of crystallization, it forms short thick and broad crystals, apparently prisms of the monoclinic system somewhat like certain felspars or rhombic crystals made up by the twinning of such prisms along one diagonal of the rhomb, and having a lemon-yellow color, which is not altered by exposure to the air. The melting point is 167°, but the white needles melt a degree and a half below this point, probably on account of the presence of the vapor of alcohol. The substance is nearly insoluble in cold water, somewhat more soluble in hot; slightly soluble in cold ethyl or methyl alcohol, more soluble in hot; very freely soluble in acetone; freely in glacial acetic acid or benzol; soluble in chloroform; slightly soluble in ether, less so in carbonic disulphide; and essentially insoluble in ligroine. The best solvent for it is boiling alcohol. The white needles, if recrystallized from chloroform or glacial acetic acid, give crystals of the lemon-yellow variety (that is free from alcohol). Strong sulphuric acid in the cold has little if any action on it, when hot it dissolves a small quantity forming a yellow solution; strong nitric acid does not dissolve it in the cold, but when hot dissolves it, forming a very pale yellowish solution; strong hydrochloric acid has no action on it, either cold or hot.

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* Hönig, Ber. d. ch. G., xi. 1041.

The dinitroresorcine dimethylether was also made from the substance melting at 237°–238° (impure bromdinitroresorcine dimethylether) by heating it to boiling with sodic methylate in methyl alcohol solution for one hour in a flask with a return condenser, at the end of which time the formation of dinitroresorcine dimethylether was proved by the melting point, 167°, and the characteristic form of the crystals. This experiment shows that the action with the methyl compounds is similar to that with the ethyl compounds already described, but it takes place less easily, since in the ethyl series heating for ten minutes was sufficient to complete the action, whereas with the methylate boiling for an hour was necessary. This formation of dinitroresorcine dimethylether furnishes us with another and most convincing proof that the substance melting at 237°–238° is essentially bromdinitroresorcine dimethylether, confirming our work with the anilido compound.

Some experiments on the action of sodic isoamylate upon tribromdinitrobenzol gave under the conditions used with the ethylate and methylate only a viscous liquid, which did not solidify even after standing for two months, and as it did not distil with steam we decided that its purification would take more time than our interest in this subject would warrant, and accordingly abandoned this branch of the research.

Action of Sodic Phenolate on Tribromdinitrobenzol.

To study this action, 30 gr. of tribromdinitrobenzol dissolved in a mixture of alcohol and benzol were mixed with an alcoholic solution of 20.8 gr. of phenol previously converted into the sodium salt by the addition of a concentrated aqueous solution of 8.8 gr. of sodic hydrate, and allowed to stand at ordinary temperatures over night. The amount of phenol used corresponds to three molecules for every molecule of the tribromdinitrobenzol. The solution turned light yellow, and deposited some crystals, apparently tribromdinitrobenzol, but the action was very limited, if any had taken place. Accordingly the mixture was heated on the steam bath in a flask with a return condenser for ten to twelve hours, when it turned dark brown, and after the solvent had been distilled off there was left in the flask a brownish viscous residue of the most uninviting appearance. This was thoroughly washed with water, and then allowed to stand for several days, which rendered it more solid; it was then washed three or four times with small quantities of cold alcohol, which removed much but not by any means all of the oily impurity, and the still viscous residue recrystallized from a mixture of alcohol and benzol until it showed the constant melting point 165°, when it was dried at 100°, and analyzed with the following results: —

I. 0.3128 gr. of the substance gave on combustion 0.5781 gr. of carbonic dioxide and 0.0790 gr. of water.

II. 0.2051 gr. of the substance gave according to the method of Carius 0.0888 gr. of argentic bromide.

	Calculated for $C_6HBr(C_6H_5O)_2(NO_2)_2$.	Found. I.	II.
Carbon	50.12	50.40	
Hydrogen	2.55	2.81	
Bromine	18.57		18.43

These results prove that the substance is the bromdinitroresorcine diphenylether. We may add, that in one preparation in addition to this a substance was obtained crystallizing in square plates and melting at about 158°, but in too small quantity for analysis, and we have not succeeded in making it again. We can say nothing about the nature of the oily product of the reaction, as we could find no way of purifying it.

Properties of Bromdinitroresorcine Diphenylether, $C_6HBr(C_6H_5O)_2(NO_2)_2$.

This substance forms woolly masses of irregularly radiating needles which under the microscope appear long and rather slender, with either a rounded sharpening at the point or else very sharp tapering ends; the substance is white at first, but turns to a pale chocolate-brown on exposure to the air. It melts at 165°, and is very slightly soluble in water whether cold or hot; slightly soluble in cold alcohol, more soluble in hot but not freely; rather more soluble in methyl than in ethyl alcohol, but not freely soluble even in this when hot; very freely soluble in chloroform; freely in benzol or acetone; soluble in ether; slightly soluble in glacial acetic acid or carbonic disulphide; very slightly soluble in ligroine. The best solvent for it is a mixture of alcohol and benzol. Neither strong sulphuric nor hydrochloric acid seemed to have any action on it, hot or cold; but strong nitric acid dissolved it after a few minutes' heating, and gave on dilution a new substance melting above 200°, probably a nitro compound. Sodic hydrate in solution has no perceptible action on the substance.

The removal of the bromine from the bromdinitroresorcine diphenylether interested us especially, as the somewhat more acid nature of the phenol radical (C_6H_5O) would we thought exercise a marked influence on it; unfortunately, however, the product has proved completely unmanageable, so that we can give only a very imperfect account of this action. We tried first hot sodic ethylate, but found that the substance was much more susceptible to its action than the corresponding ethyl or methyl compounds, showing signs of decomposition by turning dark when the mixture was heated for ten minutes; and although a less colored solution was obtained when we heated for only three or four minutes on the steam bath, the residue left after spontaneous evaporation of the alcohol was a dark-colored oily liquid which showed no signs of solidification, but gradually changed into a black tar after standing some months, and could not be brought into a state fit for analysis by any method we have been able to devise. The aqueous wash water from this substance contained sodic bromide, so that there is no question that the bromine has been removed, but we are unable to determine whether it has been replaced by hydrogen or ethoxyl.

We thought it possible that the bromine might be removed from bromdinitroresorcine diphenylether by phenol, tribromphenol being formed; but after heating the substances together on the steam bath for two days, essentially all the bromdinitroresorcine diphenylether was recovered unaltered. A mixture of sodium malonic ester with an excess of malonic ester seemed to have more effect, as the liquid turned first pale yellow and then red. It was allowed to stand in the cold for several weeks, when it was found that a small amount of sodic bromide had been formed; but the action was a very limited one, as almost all of the bromdinitroresorcine diphenylether was recovered unaltered, and the new compound was present in such small quantity that we did not succeed in isolating it.

Experiments with Tribromtrinitrobenzol.

After we had found that the bromine in bromdinitroresorcine diethylether could be replaced with hydrogen by the action of hot sodic ethylate, it became interesting to find out whether this was the same atom of bromine which undergoes a similar replacement in making bromdinitrophenylmalonic ester, that is, the atom which stands between the two nitro groups, and the easiest way to do this seemed to be to take up the study of the tribromtrinitrobenzol, in which all the atoms of bromine are similarly placed. This we have done, but without the desired result, as the sodic alcoholates show with tribromtrinitrobenzol actions entirely different from those with the corresponding dinitro compound.

Action of Sodic Ethylate on Tribromtrinitrobenzol.

To study this action 10 gr. of tribromtrinitrobenzol (symmetrical, melting at 285°) were covered with ordinary alcohol in a flask, and to the mixture of crystals and alcohol 1.6 gr. of sodium (three atoms of sodium would be a little over 1.5 gr.) previously converted into sodic ethylate was added, in small portions at a time, the flask being immersed in cold water and shaken after each addition so as to avoid a rise of temperature * in any part of the liquid. The first drop of the alcoholic solution of sodic ethylate turned red on touching the liquid in the flask, and then faded to yellow; but as the remainder of the sodic ethylate was added, the color increased in intensity, until at last it had become a deep blood-red, while at the same time the undissolved solid began to diminish in quantity, and finally entirely disappeared, leaving a clear solution, thus showing that all the tribromtrinitrobenzol had been used up, as it is nearly insoluble in alcohol. The mixture was allowed to stand over night, when it was found that a fresh amount of solid had been deposited, the solvent was then allowed to evaporate spontaneously, the residue (including the solid which had separated over night) washed with water until free from inorganic matter, and purified by crystallization from alcohol until it showed the constant melting point 101°, after which it was dried at about 70° and analyzed, with the following unexpected results: —

I. 0.3519 gr. of the substance gave on combustion 0.3427 gr. of carbonic dioxide and 0.0742 gr. of water.

II. 0.2883 gr. of the substance gave on combustion 0.2795 gr. of carbonic dioxide and 0.0632 gr. of water.

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* If the tribromtrinitrobenzol was dissolved in benzol, the action was so violent that it was almost impossible to avoid a rise of temperature.

III. 0.3165 gr. of the substance gave 9.8 c.c. of nitrogen at a temperature of 25° and a pressure of 764.7 mm.

IV. 0.2315 gr. of the substance gave by the method of Carius 0.2912 gr. of argentic bromide.

V. 0.1588 gr. of the substance gave 0.2002 gr. of argentic bromide.

	Calculated for $C_6Br_3NO_2(C_2H_5O)_2$.	Found. I.	II.	III.	IV.	V.
Carbon	26.79	26.56	26.43			
Hydrogen	2.23	2.34	2.44			
Nitrogen	3.13			3.48		
Bromine	53.57				53.55	53.64

These results show that the action is entirely different from that with tribromdinitrobenzol, for this gave with sodic ethylate bromdinitroresorcine diethylether, $C_6HBr(OC_2H_5)_2(NO_2)_2$, by the replacement of two atoms of bromine by two ethoxy radicals, whereas here under the same conditions we have the tribromnitroresorcine diethylether, which must have been formed by the replacement of two nitro groups by two ethoxy radicals. We have sought the confirmation of our analytical results, which their strangeness certainly requires, in the examination of the sodium salt formed in the reaction, which should be sodic nitrite instead of the sodic bromide which would have been formed if the reaction had run as it did with the dinitro compound. The aqueous washings from a new preparation of the substance melting at 101° gave after acidification with nitric acid only a faint turbidity with argentic nitrate, showing that only a trace of sodic bromide had been formed, whereas from other portions of the wash water we obtained the strongest reactions for a nitrite, as the following statement shows. Potassic iodide and starch paste acidified with dilute sulphuric acid gave a very deep blue color; ferrous sulphate and sulphuric acid, a brownish black color throughout the whole solution; a portion of the residue from evaporation of the wash water added to strong sulphuric acid and phenol gave a reddish brown color quickly passing through green to blue; strong sulphuric acid added to the residue from the evaporation of the wash water gave off a gas recognized as nitrous fumes by the red color and odor. There can be no doubt, therefore, that the sodic ethylate acts on tribromtrinitrobenzol according to the following reaction:—

$$C_6Br_3(NO_2)_3 + 2\,C_2H_5ONa = C_6Br_3NO_2(C_2H_5O)_2 + 2\,NaNO_2.$$

We may add, that, as we felt we could not be too careful in a case of this kind, the second specimen of tribromnitroresorcine diethylether was made from a quantity of tribromtrinitrobenzol, the purity of which had been proved by analysis in addition to the melting point, found 53.60 per cent of bromine instead of the 53.33 per cent required by the formula.

As potassium compounds behave in many respects differently from the corresponding sodium compounds, we have repeated the experiment with potassic in place of sodic ethylate, but with the same result, that is, tribromnitroresorcine diethylether melting at 101° and potassic nitrite.

Properties of Tribromnitroresorcine Diethylether, $C_6Br_3NO_2(OC_2H_5)_2$. — This substance forms well developed white flat prisms, usually with square ends, but sometimes terminated by two planes at an obtuse angle. It melts at 101°, and is very slightly if at all soluble in water, whether cold or hot; easily soluble in cold ethyl or methyl alcohol, still more freely in hot; very freely soluble in chloroform; freely in benzol; soluble in ether, acetone, carbonic disulphide, or glacial acetic acid; slightly soluble in ligroine. Hot alcohol is the best solvent for it. The three strong acids seem to have no action on it, whether they are hot or cold. Aniline dissolves it, but has no other action on it at ordinary temperatures, or even at 150°; at higher temperatures a substance similar to rosaniline is formed. A mixture of malonic ester and sodium malonic ester was allowed to stand for several weeks with an alcoholic solution of this substance; but, although at the end of this time the liquid had assumed a slight reddish color, and a little sodic bromide (but no nitrite) had been formed, the action was so limited that the only organic compound which could be detected in the product was unaltered tribromnitroresorcine diethylether melting at 101°. It appears from these experiments that the tribromnitroresorcine diethylether is not an especially reactive substance, and yet when it was boiled with an alcoholic solution of sodic ethylate a reaction took place, as was shown by the dark color which the solution assumed, and the formation of a considerable amount of sodic nitrite, proved by the test with potassic iodide, starch, and dilute sulphuric acid. Unfortunately the end of the term prevented us from isolating the organic product, or more probably products, of this reaction, but the work will be continued next year.

Tribromdinitrophenetol, $C_6Br_3(NO_2)_2OC_2H_5$.

In our first experiment on the action of sodic ethylate on tribromtrinitrobenzol the conditions were somewhat different from those described above, which gave us the tribromdinitroresorcine diethylether, since benzol was used in addition to alcohol as a solvent, and no pains were taken to cool the liquid, although the reaction produced a tolerable amount of heat. The product, which was worked up by spontaneous evaporation of the solvent, washing, and recrystallization from alcohol, showed the constant melting point 147°, instead of 101°. Upon trying to make more of this substance in the same way, we obtained a product which was evidently a mixture of the substance melting at 101° and that melting at 147°, but the end of the term has prevented us from making out the exact conditions necessary for the production of the substance melting at 147° as the principal product. Fortunately the amount of this substance made in our first experiment was sufficient for its characterization. It was dried at 100°, and analyzed with the following results: —

I. 0.1607 gr. of the substance gave on combustion 0.1237 gr. of carbonic dioxide and 0.0263 gr. of water.
II. 0.2142 gr. of the substance gave by the method of Carius 0.2683 gr. of argentic bromide.
III. 0.1736 gr. of the substance gave 0.2192 gr. of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$.	Found.		
		I	II.	III.
Carbon	21.38	20.99		
Hydrogen	1.11	1.82		
Bromine	53.46		53.31	53.74

Properties. — The tribromdinitrophenetol occurs in white, well formed, slender, nearly square prisms often a centimeter long, terminated by a single plane at an acute angle to the sides. It melts at 147°, and is soluble in cold ethyl or methyl alcohol, more freely in hot; freely soluble in benzol, chloroform, glacial acetic acid, or acetone; soluble in ether or carbonic disulphide; almost insoluble in ligroine. The best solvent for it is hot alcohol. None of the strong acids seem to have any action on it.

Action of Sodic Methylate on Tribromtrinitrobenzol.

Since sodic ethylate had acted so abnormally with tribromtrinitrobenzol, it seemed of interest to study the action of sodic methylate on this compound and accordingly we proceeded as follows.

10 gr. of tribromtrinitrobenzol in a flask were covered with absolute methyl alcohol, and the solution of sodic methylate made from 1.5 gr. of sodium was added, observing the precautions for keeping the mixture cool described under the preparation of the corresponding

ethyl compound. The first drop of sodic methylate solution turned red on touching the liquid in the flask, but this color faded to yellow as it was diffused through the solution; with continued addition of the methylate the color increased in intensity, becoming finally blood red. It seemed as if the action of the sodic methylate was more vigorous than that of the ethylate, as after about three quarters of an hour the whole of the tribromtrinitrobenzol had disappeared, leaving a clear red solution, but nevertheless the mixture was allowed to stand over night to make certain that the reaction had come to an end, after which the solvent was evaporated spontaneously, the residue washed with water (which gave a test for sodic nitrite) and crystallized from hot alcohol until it showed the constant melting point 126°, when it was dried at about 70°, and analyzed with the following results: —

I. 0.2856 gr. of the substance gave 10.1 c.c. of nitrogen at a temperature of 25° and a pressure of 755.5 mm.
II. 0.2295 gr. of the substance gave by the method of Carius 0.3072 gr. of argentic bromide.
III. 0.2311 gr. of the substance gave 0.3096 gr. of argentic bromide.

	Calculated for	Found.		
	$C_6Br_3NO_2(CH_3O)_2$.	I.	II.	III
Nitrogen	3.33	3.92		
Bromine	57.15		56.97	57.03

Properties of Tribromnitroresorcine Dimethylether, $C_6Br_3NO_2(CH_3O)_2$. — This substance crystallizes in white flattened prisms terminated usually by a single plane at a very sharp angle to the sides, rarely by two planes at an obtuse angle to each other, or also rarely the ends are square. It melts at 126°, and is nearly insoluble in cold water, perhaps a little more soluble in hot; only moderately soluble in ethyl alcohol even when hot, less soluble in it cold. It is much less soluble in alcohol than the corresponding ethyl compound; in this these two compounds resemble the methyl and ethyl compounds of the bromdinitroresorcine. Slightly soluble in cold methyl alcohol, more soluble in hot; freely soluble in benzol, chloroform, or acetone; soluble in ether, carbonic disulphide, or glacial acetic acid; very slightly soluble in ligroine. The three strong acids have no apparent action on it.

Action of Sodic Phenolate on Tribromtrinitrobenzol.

After several unsuccessful experiments we obtained satisfactory results as follows. 10 gr. of tribromtrinitrobenzol were dissolved in a mixture of benzol and ordinary alcohol, and mixed with the sodic phenolate made from somewhat more than 6.1 gr. of phenol treated with the sodic ethylate from 1.3 gr. of sodium. The slight excess of phenol was used to avoid the presence of sodic ethylate, and the salt was added in suspension in alcohol. The mixture was then heated on the steam bath under a return condenser for less than five minutes, when it had turned bright green, but was perfectly clear, and upon cooling solidified, since it became filled with loose woolly masses of radiating needles looking like thistle balls; this sudden solidification of the solution as it cools is very striking. The crystals with the residue from the mother liquors were washed with water (which took up much sodic bromide), and crystallized from a mixture of alcohol and benzol until they showed the constant melting point 175°, when they were dried at 100° and analyzed. If benzol was not used in preparing this substance, the action was only incomplete even after boiling for half an hour. The formation of sodic bromide instead of sodic nitrite, and the green instead of red color, showed that this action had gone differently from that with sodic ethylate or methylate, and this was confirmed by the following analyses : —

I. 0.2689 gr. of the substance gave on combustion 0.5823 gr. of carbonic dioxide and 0.0850 gr. of water.
II. 0.2439 gr. of the substance gave 0.5306 gr. of carbonic dioxide and 0.0775 gr. of water.
III. 0.2448 gr. of the substance gave 18.6 c.c. of nitrogen at a temperature of 23° and a pressure of 758.1 mm.

	Calculated for $C_6(C_6H_5O)_3(NO_2)_3$.	Found.		
		I.	II.	III.
Carbon	58.89	59.05	59.33	
Hydrogen	3.07	3.51	3.53	
Nitrogen	8.59			8.55

The substance was free from bromine. This action therefore has gone entirely differently from any of the others studied in this paper, consisting in the simple replacement of each bromine by one phenoxy radical (C_6H_5O), and the substance is the trinitrophloroglucine triphenylether.

Properties of the Trinitrophloroglucine Triphenylether, $C_6(NO_2)_3(C_6H_5O)_3$.

This substance crystallizes in long very slender white needles, matted together into globular woolly masses, which turn olive-brown on exposure to the air. It melts at 175°, and is essentially insoluble in water, whether cold or hot; slightly soluble in cold alcohol, more soluble in hot, but not freely; its solubility in methyl alcohol is similar to that in ethyl alcohol; very freely soluble in acetone or chloroform; freely soluble in benzol or glacial acetic acid; slightly soluble in ether or carbonic disulphide; very slightly soluble in ligroine. The three strong acids have no apparent action on it, whether hot or cold.

This is the only case in which we have observed the replacement of all three of the atoms of bromine by the radical of an alcoholate, and it is to be noted that the phenoxy radical introduced here is the most acid one which we have succeeded in introducing, whereas in the other cases where all the bromine has been replaced by the same radical this has been the alkaline amido or anilido group, —

$C_6(NH_2)_3(NO_2)_3$,* $C_6(NHC_6H_5)_3(NO_2)_3$,† $C_6H(NH_2)_3(NO_2)_2$.‡ $C_6H(NHC_6H_5)_3(NO_2)_2$.§

Experiments with Sodic Acetate, Sodic Picrate, or Sodic Nitromethane on Tribromdinitrobenzol or Tribromtrinitrobenzol.

In order to study the action of more acid radicals upon tribromdinitrobenzol we mixed 5 gr. of it with 3 gr. of sodic acetate dissolved in dilute alcohol, and, as there seemed to be no action in the cold, heated the mixture in a flask with a return condenser on the steam bath for eight hours, at the end of which time the tribromdinitrobenzol was recovered unaltered as indicated by its melting point, 192°. A similar mixture was next heated to 100° for two days in a soda-water bottle closed with an india-rubber stopper, at the end of which time 4.9 gr. of tribromdinitrobenzol melting at 192° were recovered. It is evident from these experiments that sodic acetate has no action on tribromdinitrobenzol at 100°.

As we hoped that the slighter acidity of picric acid might allow it to react on tribromdinitrobenzol, although sodic acetate would not, we next allowed 6.3 gr. of tribromdinitrobenzol to stand for a week with 12 gr. of sodic picrate suspended in alcohol, and, as at the end of this time no sodic bromide had been formed, we heated it in a flask with a return condenser on the steam bath for two days, but even after this no sodic bromide could be detected, and 6.2 gr. of tribromdinitrobenzol melting at 192° were recovered in place of the 6.3 gr.

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* These Proceedings, xxiii. 142.

† Ibid., 145.

‡ Ibid., xxiv. 106.

§ Ibid., 111.

used. Sodic picrate, therefore, does not act on tribromdinitrobenzol at 100°.

In the hope that tribromtrinitrobenzol would prove more reactive than the dinitro compound in this case, as it has in many others, the experiment was repeated with this substance, 5 gr. of tribromtrinitrobenzol to 8.3 gr. of sodic picrate mixed with alcohol and benzol being used, but after twelve hours' boiling the 5 gr. of the trinitro compound were recovered unaltered.

The sodium salt of nitromethane was also tried with tribromdinitrobenzol. 10 gr. of the latter substance dissolved in alcohol and benzol were mixed with 4.5 gr. of nitromethane previously treated with the sodic ethylate from 1.8 gr. of sodium. The mixture after standing for some time in the cold became brownish red, and the sodium salt suspended in the solution gradually disappeared, but upon working up the product 9.5 gr. of the tribromdinitrobenzol were recovered unaltered, showing that there had been no action worth considering. In a previous experiment another compound was obtained in small quantity, but we are inclined to ascribe its formation to sodic ethylate, or the products of the decomposition of the sodium salt of nitromethane rather than to that substance itself. We hope to return to this subject next year.

We had intended to include in this research the action of sodic hydrate in alcoholic solution upon tribromdinitrobenzol; but since we obtained from a preliminary experiment bromdinitroresorcine diethylether, recognized by its melting point (182° instead of 184° after one crystallization) as the principal product, we thought the subject did not promise to be of sufficient interest to repay future work.

Some preliminary experiments with mononitrotribrombenzol and sodic ethylate seemed to promise interesting results, but this part of the work must be postponed until next year.

Action of Malonic Ester on Tribromdinitrobenzol.

In previous papers * of this series it has been proved that in the formation of bromdinitrophenylmalonic ester from sodium malonic ester and tribromdinitrobenzol the bromine atom replaced by hydrogen stands between two nitro groups. In view of this fact, it seemed desirable to determine whether the ease with which this atom of bromine was removed by the action of malonic ester depended only on this position, and experiments were tried and described in a previous paper * which seemed to disprove this view. On returning to the subject, this point seemed to us of so much importance that we determined to repeat the experiment, especially as the conditions under which the malonic ester acted on the tribromdinitrobenzol in the earlier work were not exactly the same as those of the action of the sodium malonic ester in the preparation of bromdinitrophenylmalonic ester; accordingly, in repeating the experiment as described below we have reproduced these conditions as exactly as possible, except that malonic ester was used in place of sodium malonic ester.

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* These Proceedings, xxiv. 248, 250 (1889).

To 4 gr. of malonic ester dissolved in 30 c.c. of absolute alcohol were added 5 gr. of tribromdinitrobenzol dissolved in anhydrous benzol, and the mixture was allowed to stand in the cold for three or four days, at the end of which time, there being no signs that a reaction had taken place, the solvent was allowed to evaporate spontaneously, and the malonic ester mother liquor poured off from the crystals, which after careful drying on a steam radiator at about 70° weighed 3.4 gr. and melted at 192° (the melting point of tribromdinitrobenzol). The mother liquor was allowed to stand in a loosely covered dish for a month, when the malonic ester had evaporated, leaving an additional crop of crystals, which after drying as before weighed 1.75 gr., and also showed the melting point of the tribromdinitrobenzol. So that the weight of the recovered tribromdinitrobenzol was 5.15 gr. † This experiment therefore confirms those previously tried,* and proves conclusively that malonic ester has no action upon tribromdinitrobenzol ($BrNO_2BrNO_2BrH$), and consequently that the replacement of the bromine atom by hydrogen in the formation of bromdinitrophenylmalonic ester depends on other conditions in addition to the influence of the nitro groups and other bromine atoms upon it. The discussion of these other conditions will be postponed until we have collected more experimental material.

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* These Proceedings, xxiv. 308 (1889).

† The slight excess (0.15 gr.) over the amount used is easily accounted for by the dust which during the long standing found its way into the loosely covered evaporating dish.